Claims

1. An electrode for use in a electrochemical sensor, said electrode comprising carbon and a redox-active compound, excluding an electrode based on carbon having derivatised thereon two redox-active species wherein at least one of said species is selected from anthraquinone, phenanthrenequinone or N,N□¥diphenyl-*p*-phenylenediamine (DPPD).

2. An electrode according to claim 1, wherein the redox active compound is not anthraquinone, phenanthrenequinone or N,N□-diphenyl-*p*-phenylenediamine.

3. An electrode according to claim 1 or claim 2, wherein the redox active compound is a chemically sensitive compound.

4. An electrode according to any of the preceding claims wherein the carbon and the redox-active compound are formulated together prior to formation of the electrode.

5. An electrode according to any of the preceding claims wherein the carbon is modified by one or more of the following methods:

1) homogeneous chemical derivatisation with the chemically sensitive redox active material;
2) derivatisation via physical adsorption of the chemically sensitive redox active material; and
3) physical mixing with the chemically sensitive redox active material and a binder.

6. An electrode comprising carbon modified with a redox active material, wherein the redox active material undergoes an irreversible chemical reaction when the electrode is

subjected to cyclic voltammetry.

7. An electrochemical sensor comprising an electrode as claimed in any of the preceding claims.

8. A pH sensor comprising:

a working electrode comprising carbon modified with a chemically sensitive redox active material; and

a counter electrode,

wherein the ratio of the surface area of the working electrode to the surface area of the counter electrode is from 1:10 to 10:1.

9. A pH sensor according to claim 8 wherein the surface area of the working electrode is from $10\mu m^2$ to $0.1m^2$.

10. A pH sensor according to claim 9 wherein the surface area of the working electrode is from $50\mu m^2$ to $0.1m^2$.

11. A pH sensor comprising:

a working electrode comprising carbon modified with a chemically sensitive redox active material, and

a counter electrode,

wherein the area of the working electrode is from $500\mu m^2$ to $0.1m^2$.

12. A pH sensor according to any one of claims 8 to 11 wherein the ratio of the surface area of the working electrode to the surface area of the counter electrode is from 1:5 to 3:1.

13. A pH sensor according to any one of claims 8 to 12 wherein the surface area of the working electrode is from 0.5mm^2 to 10mm^2.

14. A pH sensor according to any one of claims 8 to 13 wherein the chemically sensitive redox active material is sensitive to a change in pH.

15. A pH sensor according to claim 14 wherein the carbon is modified by one or more of the following methods:

1) homogeneous chemical derivatisation with the chemically sensitive redox active material;
2) derivatisation via physical adsorption of the chemically sensitive redox active material; and
3) physical mixing with the chemically sensitive redox active material and a binder.

16. A pH sensor according to any one of claims 8 to 15 wherein the working electrode further comprises at least chemically insensitive redox active material.

17. A pH sensor according to any one of claims 8 to 16 wherein the chemically sensitive redox active material comprises more than one different compound.

18. A pH sensor according to claim 17 wherein the working electrode comprises two redox active materials which are sensitive to a change in pH and two redox active materials which are insensitive to a change in pH.

19. A pH sensor according to any one of claims 14 to 18 wherein the chemically sensitive redox active material undergoes an irreversible chemical reaction when the electrode is subjected to cyclic voltammetry.

20. A pH sensor according to claim 17 wherein the product of the irreversible chemical reaction displays reversible electrochemistry when the electrode is subjected to cyclic voltammetry.

21. A method for preparing an electrode for use in an electrochemical sensor, said method comprising modifying carbon with a chemically sensitive redox active material with the proviso that the chemically sensitive redox active material is not two redox active species one of which is selected from anthraquinone, phenanthrenequinone or N,N'-diphenyl-*p*-phenylenediamine (DPPD).

22. A method according to claim 21 wherein the step of modifying the carbon comprises one or more of the following methods:

1) homogeneous chemical derivatisation with the chemically sensitive redox active material;
2) derivatisation via physical adsorption of the chemically sensitive redox active material; and
3) physical mixing with the chemically sensitive redox active material and a binder.

23. A method according to claim 21 or 22 wherein the chemically sensitive redox active material undergoes an irreversible chemical reaction when subjected to cyclic voltammetry.

24. A method according to claim 23 wherein the product of the irreversible chemical reaction displays reversible electrochemistry when the electrode is subjected to cyclic voltammetry.

25. A method according to any one of claims 21 to 24 further comprising the step of applying the carbon modified with the chemically sensitive redox active material to a

substrate.

26. A method according to any one of claims 19 to 23 wherein the chemically sensitive redox active material is sensitive to a change in concentration of hydrogen ions.

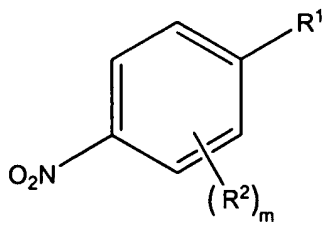
27. A method for preparing an electrode *in situ* comprising applying carbon modified with a chemically sensitive redox active material to the surface of a substrate, wherein the chemically sensitive redox active material undergoes an irreversible chemical reaction when subjected to cyclic voltammetry.

28. A method according to claim 27 wherein the product of the irreversible chemical reaction displays reversible electrochemistry when the electrode is subjected to cyclic voltammetry.

29. A method according to claim 27 or claim 28 wherein the chemically sensitive redox active material undergoes polymerisation when subjected to cyclic voltammetry.

30. A method according to claim 28 or claim 29 wherein the chemically sensitive redox active material has a nitro group substituent.

31. An electrode according to any of claims 1 to 6 or forming part of a pH sensor according to any of claims 8 to 20 and comprising, disposed on a substrate, a composition comprising carbon and a compound of formula (I):



(I)

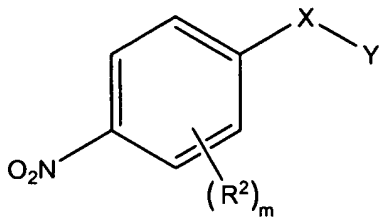
wherein

- R^1 represents a group of formula -Y or -X-Y wherein Y is selected from hydrogen, hydroxy, C_{1-4} alkyl and $-NR^3R^4$ wherein R^3 and R^4 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy, and wherein X represents a group of formula $-(CR^5R^6)_n-$ wherein n is 0 or an integer from 1 to 4 and R^5 and R^6 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl, C_{1-4} alkoxy or R^5 and R^6 together form a group of formula =O or $=NR^7$ wherein R^7 is selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy;
- R^2 is selected from hydroxy, halogen, C_{1-4} alkyl, C_{2-4} alkenyl, C_{1-4} alkoxy, C_{2-4} alkenyloxy, amino, C_{1-4} alkylamino, di(C_{1-4} alkyl)amino; C_{1-4} alkylthio, C_{2-4} alkenylthio, nitro, cyano, -O-CO-R′, -CO-O-R′, -CO-NR′R′′, -COR′, -S(O)R′ and $-S(O)_2R'$, wherein each R′ and R′′ is the same or different and represents hydrogen, C_{1-4} alkyl or C_{2-4} alkenyl; and
- m is 0 or an integer from 1 to 4;

or salts thereof, wherein said compound of formula (I) is partially intercalated within the carbon.

32. An electrode according to claim 31 where the powdered carbon is in the form of graphite or multi-walled carbon nanotubes.

33. An electrode according to claim 31 and claim 32 wherein the compound is a nitrobenzene derivative of formula (II):



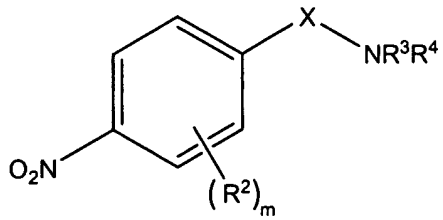
(II)

wherein:

- R^2 is selected from hydroxy, halogen, C_{1-4} alkyl and C_{1-4} alkoxy;
- m is 0, 1 or 2;
- X represents a group of formula $-(CR^5R^6)_n-$ wherein n is 0, 1 or 2 and R^5 and R^6 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy; and
- Y is selected from hydrogen, hydroxy, C_{1-4} alkyl and $-NR^3R^4$ wherein R^3 and R^4 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy,

or a salt thereof.

34. An electrode according to any of claims 31 to 33 wherein the compound is a nitrobenzene derivative of formula (III):



(III)

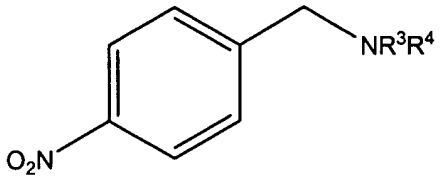
wherein:

- R^2 is selected from hydroxy, halogen, C_{1-4} alkyl and C_{1-4} alkoxy;
- m is 0, 1 or 2;
- X represents a group of formula $-(CR^5R^6)_n-$ wherein n is 0, 1 or 2 and R^5 and R^6 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy; and

- R^3 and R^4 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy,

or a salt thereof.

35. An electrode according to any of claims 31 to 34 wherein the compound is a nitrobenzene derivative of formula (IV):



(IV)

wherein R^3 and R^4 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy, or a salt thereof.

36. An electrochemical sensor comprising a working electrode and a counter electrode, wherein the working electrode comprises an electrode as claimed in any of claims 31 to 35.

37. A sensor according to claim 36 and further comprising a reference electrode.

38. A method for preparing an electrode for use in an electrochemical sensor, said method comprising providing a substrate and applying a composition defined in claim 31 to the surface of said substrate.

39. The method of claim 38 wherein the step of applying comprises abrasively immobilising the composition on the surface of the substrate.

40. An electrode according to any of claims 1 to 6 or forming part of a pH sensor according to any of claims 8 to 20 wherein said electrodes comprises, disposes on a substrate, carbon nanotubes and a redox active material.

41. An electrode according to claim 40 wherein the redox active material has a voltammetric response which is chemically sensitive to the concentration of the species to be detected by the electrochemical sensor.

42. An electrode according to claim 40 or claim 41 wherein the redox active material is sensitive to the concentration of protons.

43. An electrode according to any one of claims 40 to 41 wherein the redox active material comprises a further redox active material which is chemically insensitive to the concentration of the species to be detected by the electrochemical sensor.

44. An electrode according to any one of claims 40 to 43 wherein the redox active material comprises at least two redox active materials chemically sensitive to the concentration of the species to be detected by the electrochemical sensor.

45. An electrode according to any of claims 40 to 44 wherein the carbon nanotubes and redox active material are applied to the substrate either in the form of a mechanical mixture, or in the form of an agglomerate.

46. An electrode according to claim 45 wherein the agglomerate is abrasively immobilised on the substrate.

47. An electrochemical sensor comprising a working electrode and a counter electrode,

wherein the working electrode comprises the electrode as defined in any one of claims 40 to 46.

48. A sensor according to claim 47 further comprising a reference electrode.

49. A sensor according to claim 48, wherein the redox active material is sensitive to the concentration of protons and the sensor is a pH sensor.

50. A method for preparing an electrode for use in electrochemical sensors, said method comprising providing a substrate and applying carbon nanotubes and a redox active material to the surface of said substrate.

51. A method according to claim 50 wherein the carbon nanotubes and redox active material are applied to the substrate in the form of a mechanical mixture, or in the form of an agglomerate.

52. A method according to claim 50 or claim 51 wherein the step of applying comprises abrasively immobilising the carbon nanotubes and redox material on the substrate.

53. A method according to claim 51 wherein the method comprises the steps of:

1. combining the carbon nanotubes and a binder in a solvent;
2. adding an excess of aqueous solution such that the agglomerate is precipitated out of the solvent; and
3. recovering the agglomerate.

54. An electrode according to any of claims 1 to 6, or forming part of a pH sensor

according to any of claims 8 to 20, wherein the electrode comprises a layer on a substrate of a composition of said carbon and said redox-active compound, said layer having an edge formed by cutting through said layer to expose carbon and redox-active compound.

55. An electrode according to claim 54 wherein the layer comprises a mixture of a carbon-based ink and said redox-active compound.

56. An electrode according to claim 54 or claim 55 wherein the redox-active compound is in the form of crystals.

57. An electrode according to any of claims 54 to 56 wherein the redox-active compound is phenanthrenequinone.

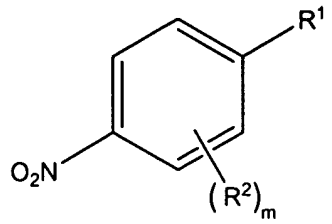
58. An electrochemical sensor comprising a working electrode and a counter electrode, wherein the working electrode comprises the electrode as claimed in any of claims 54 to 57.

59. Use of an electrode as claimed in any of claims 1 to 6, 31 to 35, 40 to 46 and 52 to 57 in an electrochemical sensor.

60. Use according to claim 59 wherein the sensor is a pH sensor.

61. Use of a sensor as claimed in any of claims 8 to 20, 36, 37, 47 to 49 and 58 in a non-downhole environment.

62. A method of modifying carbon by the partial intercalation of a compound which is a nitrobenzene derivative of formula (I):



(I)

wherein

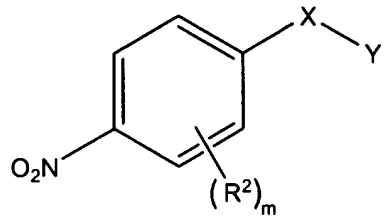
- R^1 represents a group of formula -Y or -X-Y wherein Y is selected from hydrogen, hydroxy, C_{1-4} alkyl and $-NR^3R^4$ wherein R^3 and R^4 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy, and wherein X represents a group of formula $-(CR^5R^6)_n-$ wherein n is 0 or an integer from 1 to 4 and R^5 and R^6 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl, C_{1-4} alkoxy or R^5 and R^6 together form a group of formula =O or $=NR^7$ wherein R^7 is selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy;
- R^2 is selected from hydroxy, halogen, C_{1-4} alkyl, C_{2-4} alkenyl, C_{1-4} alkoxy, C_{2-4} alkenyloxy, amino, C_{1-4} alkylamino, di(C_{1-4} alkyl)amino; C_{1-4} alkylthio, C_{2-4} alkenylthio, nitro, cyano, -O-CO-R′, -CO-O-R′, -CO-NR′R′′, -COR′, -S(O)R′ and $-S(O)_2R'$, wherein each R′ and R′′ is the same or different and represents hydrogen, C_{1-4} alkyl or C_{2-4} alkenyl; and
- m is 0 or an integer from 1 to 4;

or a salt thereof, which method comprises mixing powdered carbon with a compound as defined above for a time sufficient to allow the compound to partially intercalate within the carbon, and isolating the resulting modified carbon.

63. The method of claim 62 wherein the powered carbon and compound are mixed in a solvent, said solvent being an aprotic organic solvent.

64. The method of claim 62 or claim 63 wherein the powdered carbon is in the form of graphite or multi-walled carbon nanotubes.

65. The method of any of claims 62 to 64 wherein the compound is a nitrobenzene derivative of formula (II):



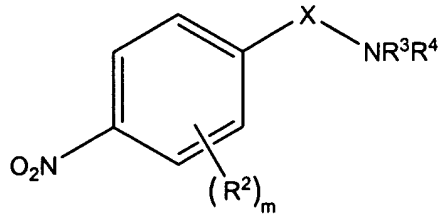
(II)

wherein:

- R^2 is selected from hydroxy, halogen, C_{1-4} alkyl and C_{1-4} alkoxy;
- m is 0, 1 or 2;
- X represents a group of formula $-(CR^5R^6)_n-$ wherein n is 0, 1 or 2 and R^5 and R^6 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy; and
- Y is selected from hydrogen, hydroxy, C_{1-4} alkyl and $-NR^3R^4$ wherein R^3 and R^4 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy,

or a salt thereof.

66. The method of claim 65 wherein the compound is a nitrobenzene derivative of formula (III):



(III)

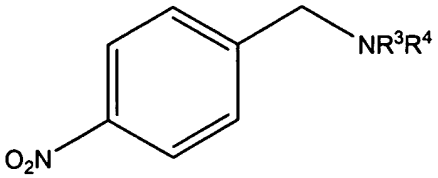
wherein:

- R^2 is selected from hydroxy, halogen, C_{1-4} alkyl and C_{1-4} alkoxy;
- m is 0, 1 or 2;

- X represents a group of formula $-(CR^5R^6)_n-$ wherein n is 0, 1 or 2 and R^5 and R^6 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy; and
- R^3 and R^4 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy,

or a salt thereof.

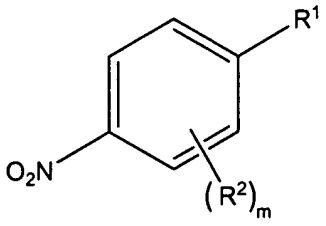
67. The method of claim 66 wherein the compound is a nitrobenzene derivative of formula (IV):



(IV)

wherein R^3 and R^4 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy, or a salt thereof.

68. A composition comprising carbon and a compound of formula (I):



(I)

wherein

- R^1 represents a group of formula -Y or -X-Y wherein Y is selected from hydrogen, hydroxy, C_{1-4} alkyl and $-NR^3R^4$ wherein R^3 and R^4 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy, and wherein X represents a group of formula $-(CR^5R^6)_n-$ wherein n is 0 or an integer from 1 to 4 and R^5 and R^6 are the same or different and are selected from hydrogen, hydroxy, C_{1-4} alkyl, C_{1-4} alkoxy or R^5 and R^6 together form a

group of formula =O or =NR^7 wherein R^7 is selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy;

- R^2 is selected from hydroxy, halogen, C_{1-4} alkyl, C_{2-4} alkenyl, C_{1-4} alkoxy, C_{2-4} alkenyloxy, amino, C_{1-4} alkylamino, di(C_{1-4} alkyl)amino; C_{1-4} alkylthio, C_{2-4} alkenylthio, nitro, cyano, -O-CO-R′, -CO-O-R′, -CO-NR′R′′, -COR′, -S(O)R′ and -$S(O)_2$R′, wherein each R′ and R′′ is the same or different and represents hydrogen, C_{1-4} alkyl or C_{2-4} alkenyl; and
- m is 0 or an integer from 1 to 4;

or salts thereof, wherein said compound of formula (I) is partially intercalated within the carbon.

69. A composition according to claim 68 wherein the carbon is in the form of graphite or multi-walled carbon nanotubes.

70. A composition according to claim 68 or 69 wherein the compound of formula (I) is as defined in any one of claims 4 to 6.

71. An agglomerate for use in electrochemical sensors, said agglomerate comprising carbon nanotubes dispersed in a binder, wherein the binder is a redox active material.

72. An agglomerate according to claim 71 wherein the redox active material has a voltammetric response which is chemically sensitive to the concentration of the species to be detected by the electrochemical sensor.

73. An agglomerate according to claim 71 or claim 72 wherein the redox active material is sensitive to the concentration of protons.

74. An agglomerate according to any one of claims 71 to 73 wherein the redox active material comprises a further redox active material which is chemically insensitive to the concentration of the species to be detected by the electrochemical sensor.

75. An agglomerate according to any one of claims 71 to 74 wherein the redox active material comprises at least two redox active materials chemically sensitive to the concentration of the species to be detected by the electrochemical sensor.

76. Use of an agglomerate according to any of claims 71 to 75 or of an electrode according to any of claims 6 to 10 in an electrochemical sensor.